

LeS B.1 Sediments & river systems

CONTAMINATED RIVER SEDIMENTS: POTENTIAL CHEMICAL TIME BOMBS? A CASE STUDY

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1 Introduction

Dredging of waterways is necessary to keep waterways navigable and to prevent rivers from flooding. In the next few decades, Europe faces the large-scale remediation of historically contaminated areas of sedimentation in many river catchments. Within the European Water Framework Directive, there is a growing concern of the need of sediment quantity and quality management. The understanding of the behaviour and fate of contaminants in sediments and dredged materials is essential to deal with the management of contaminated sediments (SedNet, 2003).

In Flanders (northern Belgium) more than 50% of the navigable waterways and 30% of the non-navigable waterways are severely polluted with heavy metals and organic pollutants (Vlaamse Milieumaatschappij, 2003; OVAM 2003). Besides the yearly accumulation of contaminated sediments, which is estimated to be around 1.3 million metric ton (dry matter), Flanders faces a considerable historic backlog of about 23.6 million metric ton of sediment (dry matter) (OVAM, 2003)).

Heavy metal mobility is of major concern in ecological evaluations. Especially in systems involving solid-solution interactions it is important to know how heavy metal mobility is influenced by geochemical processes. Besides the information on actual heavy metal mobility, predictions about the long-term behaviour of pollutants are necessary to perform a risk assessment. Therefore, the capacity controlling parameters (CCP's) have to be taken into account since they control geochemical and microbiological processes that determine the fate of pollutants in soils and sediments (Stigliani et al., 1991). CEC, pH, redox potential, soil organic matter, salinity and microbiological activity are the CCP's of soils and sediments for heavy metals. With respect to heavy metals, there are two modes in which saturation of soils and sediments occur, with subsequent triggering of chemical time bombs (Hekstra, 1995). The first is direct saturation, by which the capacity of a soil or sediment for toxic chemicals becomes exhausted. The second way to "trigger" a time bomb is through a fundamental change in a chemical property of the substrate that reduces its capacity to adsorb (or keep adsorbed) toxic materials.

With respect to dredged material, the most important process that can cause a release of heavy metals is the oxidation of anoxic sediments. Additionally, alluvial soils and sediments with a low ANC are vulnerable for acidification (Kuiper, 1996). Japenga and Salomons (1993), who analysed contaminated sediments deposited in the Rhine floodplain, mention that the high organic matter-, calcium carbonate- and clay-content of the sediments caused the contaminants to remain tightly bound to the sediments. Nevertheless, they point to the fact that changes which reduce the organic matter or calcium carbonate content may enhance the bioavailability and leaching of contaminants. A more detailed knowledge of capacity

controlling parameters can be helpful to take adequate measures in land management or to restrict certain types of land use in vulnerable areas.

According to the Flemish environmental legislation, contaminated sediments can be stored along a waterway, inasmuch the concentrations of contaminants are below threshold values (OVAM, 2003). When contamination is less than 80% of the Intervention Values for soil contamination, the dredged material can be stored along the river for a period of maximum 2 months. For urgent dredging operations, this criterion has not to be fulfilled, but a risk assessment study is compulsory and the sediment has to be removed within two months.

According to Borma et al. (2003), it is extremely difficult to assess the medium- and long-term mobility of heavy metals from land-disposed dredged sediments from laboratory tests. Several researchers performed water extractions during sediment ripening (Singh et al., 2000; Stephens et al., 2001) or monitored porewater composition (Prokop et al., 2003). Although this approach is useful to assess the medium-term (up to several months) mobility of metals, it is not adequate when a quick decision has to be made concerning the potential impact of dredging and land-disposal of contaminated sediments.

In the present paper, the consequences of dredging and land-disposal of two (strongly) contaminated sediments were investigated. Porewater composition was monitored during sediment ripening. In addition, to increase the oxidation rate of the anoxic sediment, a resuspension experiment was performed and the ability of this test to predict the evolution of porewater composition and sediment properties was evaluated.

2 Methodology

2.1 Sampling

The selection of the sampling locations was based on the database of river sediments in Flanders (Vlaamse Milieumaatschappij, 2003). This database contains data on 450 riverbed samples that were evaluated on a physico-chemical, biological and ecotoxicological basis according to the TRIADE method. The Upper Scheldt (US) in Kluisbergen and the Kogbeek (KB) in Dilsen-Stokkem (Flanders, N-Belgium) and were selected as sampling location because of their very bad global (physico-chemical, biological and ecotoxicological) sediment quality. The Upper Scheldt is the upstream part of the Scheldt river (catchment area = 21 600 km²), which is one of the major rivers in Flanders (N-Belgium). River sediments of the Scheldt are polluted by waste water emission from industry, households and agriculture. The Kogbeek river, which is approximately 5 km long, is a tributary of the Meuse river. Heavy metal pollution of the Kogbeek is principally caused by the wastewater emission of a plant for the treatment of Zn- and Pb-ores. In October 2003, Van Thuyne and Breine (2003) monitored the fish assemblage of 11 tributaries of the Meuse river and did not find any fish in the Kogbeek river.

The sediments were sampled in October (Upper Scheldt) and November (Kogbeek) 2003 with a Van Veen grab and transported to the laboratory in a sealed container, whereafter experiments immediately started. Approximately 3 L of wet sediment was placed in a polyethylene container (Ø 20 cm, 15 cm high) in which Rhizon Soil Moisture Samplers (Rhizon SMS, Eijkelkamp, The Netherlands) were inserted horizontally at a distance of 2 and 10 cm from the sediment surface respectively. The Rhizon SMS causes minimal disturbance of the sediment and has the advantage that it can be left in place throughout the entire experiment duration. Porewater was extracted every day during the first week and subsequently 3 times a week during 59 (Upper Scheldt) and 35 (Kogbeek) days. On day 15, 29 and 35 the sediment was rewetted to simulate a rainfall event (2.3, 3.5 and 3.5 L m⁻² respectively).

2.2 Physico-chemical sediment characterisation

The water content of the sediment was calculated by weight difference before and after drying at 105°C. Organic carbon was determined according to the Walkey and Black method (Nelson and Somers, 1986). Total sulphur was determined with the Ströhlein Sulfur Analyzer (model S-mat, Carbolite Co. Ltd., Bamford-Sheffield). Grain size was determined by laser diffraction analysis (Malvern® Mastersizer S long bed) and cation exchange capacity (CEC) was analyzed applying the 'silver thiourea method' (Chhabra et al., 1975). Total element concentrations (Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, K, Ni, Pb and Zn) were determined in all the samples. The term 'total' is used here as the amount of metals dissolved according to the 3 acid dissolution method. Therefore, one gram of each sample was dissolved in a 3-acid mixture (4 mL HCl_{conc}, 2 mL HNO_{3conc} and 2 mL HF_{conc}) in a Teflon beaker. The mixture was gently heated on a hot plate until half dry and subsequently reattacked with the same three acids and heated until completely dry. The residue was redissolved with 20 mL 2.5 N HCl and filtered (Whatman 45). Finally, the solution was diluted to 50 mL with distilled water. These solutions were analyzed by AAS (Varian Techtron AA6) for Zn, Ca, Fe, K, Mg and Al and by ICP-MS (HP 4500 series) for As, Cd, Cr, Cu, Ni, Pb and Mn (see 2.4). A certified reference material (GBW07411 Soil) and sample duplicates were used for quality control. Values (in mg kg⁻¹) obtained were for Cd: 25.9 (certified value 28.2 ± 1.3), Zn: 3630 (certified value 3800 ± 300), Ni: 22.3 (certified value: 24.2 ± 2.1), Cu: 62.9 (certified value 65.4 ± 4.7) and Pb: 2810 (certified value 2700 ± 100). All reagents used for analysis were of analytical grade. All glassware was acid rinsed with HNO₃ 0.2 M before usage. To check accuracy, all the analysis were performed in triplicate.

2.3 Resuspension experiment

For the resuspension experiments, ±220 g of wet sediment (equivalent to 80 g of dry sediment) was put in an Erlenmeyer flask of 1 L together with 660 mL of distilled water and placed on an horizontal shaking device. A pH-electrode (pH Hamilton Single pore electrode) and a redox electrode (Mettler Toledo Pt 4805-S7/165 Combination redox electrode) were attached to the flask. At regular time intervals (0, 0.5, 1, 3, 6, 12, 24, 48, 72, 96, 168 and 192 h for both sediments, plus at 216 and 240 h for sediment KB), a sample of the suspension was taken over a filter (0.45 µm Acrodisc, Pall) by means of a syringe attached to a flexible tube (for more details see also Van Herreweghe *et al.*, (2002) and Cappuyns *et al.* (2004a)). The resuspension was performed until more or less a stable pH was reached. Immediately after sampling, the sample was acidified with a drop of concentrated HNO₃ (ultrapure) to bring the pH < 2. Subsequently the sample was kept in a refrigerator until analysis.

2.4 Analysis

In the porewater and the suspension samples, sulfate was measured by turbidimetry (Vogel, 1961). For the ICP-MS analysis (HP4500), the samples were diluted with 5% HNO₃ (ultrapure). Standard series were made up starting from the '10ppm Multi-Element Calibration Standard-2A in 5% HNO₃' (Hewlett Packard, Palo Alto, CA). An Indium (In) internal standard was applied to both samples and standards. The spectroscopic interference of ArCl, which has the same m/z as As (75) was corrected according to the recommendations of the EPA (method 200.8, Brockhoff et al., 1999). Each ICP-MS measurement was carried out with three repetitions holding relative standard deviations below five percent. Standard deviation between triplicate extractions was less than 5 %. Accuracy was also checked by measuring standard solutions as unknown samples.

In the final pH_{stat} leachates, dissolved organic carbon (DOC) was measured with a TOC analyser (Schimadzu TOC-500). Electrical conductivity (18.34 EC-meter, Eijkelkamp) and redox potential (Mettler Toledo Pt 4805-S7/165 Combination redox electrode) were also determined.

3 Results

3.1 General sample characteristics

Sediment KB is highly polluted with Zn, Ni, Cd, Cu, Cr and Pb and characterised by an elevated S- and organic carbon-content (Table 1). It is mainly composed of silt and the major mineralogical phases are quartz, illite and kaolinite. Intervention Values for Soil Contamination, corrected for the organic carbon- and clay-content, were calculated for both sediments (OVAM, 1995). Sediment KB is contaminated with Zn, Ni, Cd, Cr, Cu and Pb, with total concentrations 4 to 20 times above Intervention Values for soil contamination. Sediment US is characterised by an elevated clay-, organic carbon, and CaCO₃-content (Table 1). Zn, Cd and Cr are the main contaminants in sediment US

Table 1 Concentrations of major and trace elements, organic carbon content (OC), CEC (mean \pm standard deviation of 3 replicates) and grainsize of samples KB and US. Intervention Values for soil contamination (I.V.) were calculated for each sediment.

	Zn	Ni	Cd	Cu	Cr	Pb	Mn			
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg			
KB	11544 \pm 241	658 \pm 33	23 \pm 2	7163 \pm 251	2047 \pm 14	1797 \pm 73	179 \pm 9			
US	1851 \pm 53	43 \pm 2.7	8.0 \pm 0.1	101 \pm 9.1	254 \pm 7.2	112 \pm 38	634 \pm 11			
I.V. KB	1050	179	4.8	271	172	349				
I.V. US	1140	202	5.6	327	206	331				
	Ca	Fe	Al	OC	S	CEC	clay	silt	sand	
	%	%	%	%	%	cmol/kg	%	%	%	
KB	2.46 \pm 0.1	5.4 \pm 1	2.2 \pm 0.3	12.5 \pm 0.8	3.6 \pm 0.8	21.9 \pm 0.8	30	43	27	
US	4.26 \pm 0.2	3.26 \pm 0.06	3.9 \pm 0.3	8.9 \pm 0.4	0.76 \pm 0.4	34.1 \pm 1.0	46	47	7	

3.2 Heavy metal release into the porewater upon oxidation

3.1.1 Kogbeek

The anoxic sediment KB had an initial water content of 65% and was characterised by a slightly alkaline pH. Upon oxidation, pH decreased to reach a value of 3.9 after 39 days (Fig. 1). 3 stages could be distinguished in the evolution of the pH of the porewater with time (Fig. 1). pH was initially 7.5-7.8 and remained around 7 during the first 6 days (stage I). After this more or less constant stage, a linear decrease in pH was observed until day 20, when a pH-value of 4 was reached (stage II). Finally, pH decreased slowly from 4 to 3.5 during the following 17 days (stage III).

Fe-, Al- and heavy metal concentrations in the porewater increased with an order of magnitude from stage I tot stage II and from stage II to stage III. Ca-concentrations increased during the first 8 days (2 cm from the surface) or 13 days (10 cm the from surface) of oxidation, followed by a concentration decrease.

The considerable pH-decrease during oxidation (Fig. 1) points to the low acid neutralising capacity of the sediment. The pH decrease is due to chemical oxidation and intensified by the activity of *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* (Calmano et al., 1993, Lors et al., 2004). SO₄²⁻-concentrations in the porewater increased from 187 \pm 20 mg/L on day 1 to 17761 \pm 2734 mg/L on day 39. The most important increase in SO₄²⁻- concentrations was observed between day 6 and day 20 (stage II).

Heavy metal release into the porewater was rather limited in stage I (Fig. 1). During stage II, Zn-, Ni-, Cd-, Cu-, Pb-, Cr- and Co-concentrations increased with more than 3 orders of magnitude. The rate of metal leaching most significantly increased between day 8 and 13, when pH dropped from 7.2 to 5.5.

3.1.2 Upper Scheldt

Sediment US had an initial water content of 72%. Oxidation and ripening resulted in the loss of water due to evapotranspiration, the formation of cracks and subsidence of the surface and colour changed from black (2.5Y2/1) to dark greyish yellow (2.5Y4/2). On day 24, the sediment was completely oxidised. The pH of the porewater was rather constant during the 2 months of ripening (Fig. 1), with an average value of 7.4 ± 0.3 in the upper part and 7.5 ± 0.3 in the lower part of the sediment.

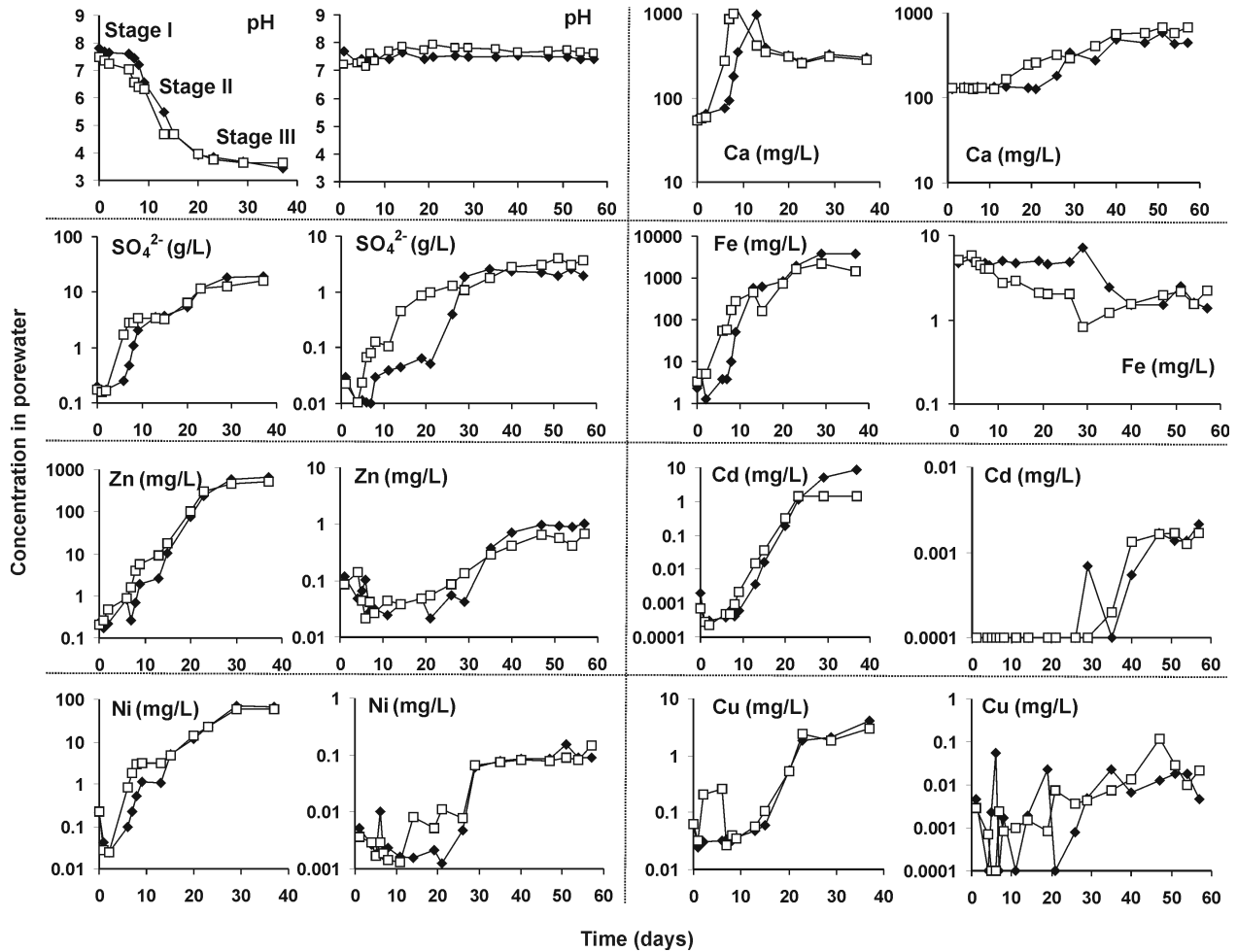


Figure 1: Evolution of pH and Ca-, SO₄²⁻, Fe-, Zn-, Cd-, Ni- and Cu-concentrations in the porewater upon oxidation of sediment KB (left picture) and US (right picture) at 2 cm (open symbols) and 10 cm (closed symbols) from the sediment surface.

Fe-concentrations decreased with time and the decrease was faster in the upper part of the sediment (2 cm from sediment surface) than deeper in the sediment (10 cm from the surface) (Fig. 1). Sulphate concentrations in the porewater were characterised by a considerable increase after 11 and 19 days in the upper and lower part of the sediment respectively. Higher sulphate concentrations were generally found closer to the sediment surface.

During the first 29 days of simulated land-disposal, Zn-concentrations between 22 and 118 µg/L were measured in the porewater (Fig. 1). On day 35, a considerable increase of Zn-concentrations was detected. Cd appeared in the porewater on day 26, after which its concentrations also showed an almost continuous increase with time. Similarly, Ni exhibited a rather sudden release into the porewater on day

35. The evolution of Cu-concentrations in the porewater with time was not characterised by a particular pattern.

3.3 Metal release upon resuspension

3.1.1 Kogbeek

During resuspension of the anoxic sediment KB, redox potential increased from -67 to 483 mV, while pH decreased from 8.2 to 3.5 (Fig. 2). The pattern of pH-decrease was similar as for the porewater (Figs. 1 and 2). Apparently, during resuspension, the oxidation rate was enhanced with a factor of ± 4 compared to the simulated deposition of the sediment on land. The suspension of the sediment in water and the continuous agitation of the suspension result in a faster oxygenation of the sediment.

The sharp pH-drop to pH 5.3 at $t = 48$ h is accompanied by an important release of Zn and Ni, whereas Cd and Cr are only released after 168 h, when pH decreases below 4 (Fig. 2).

During resuspension, a significant release of Fe (more than 1000 mg/kg) is only observed after the pH dropped below 5.

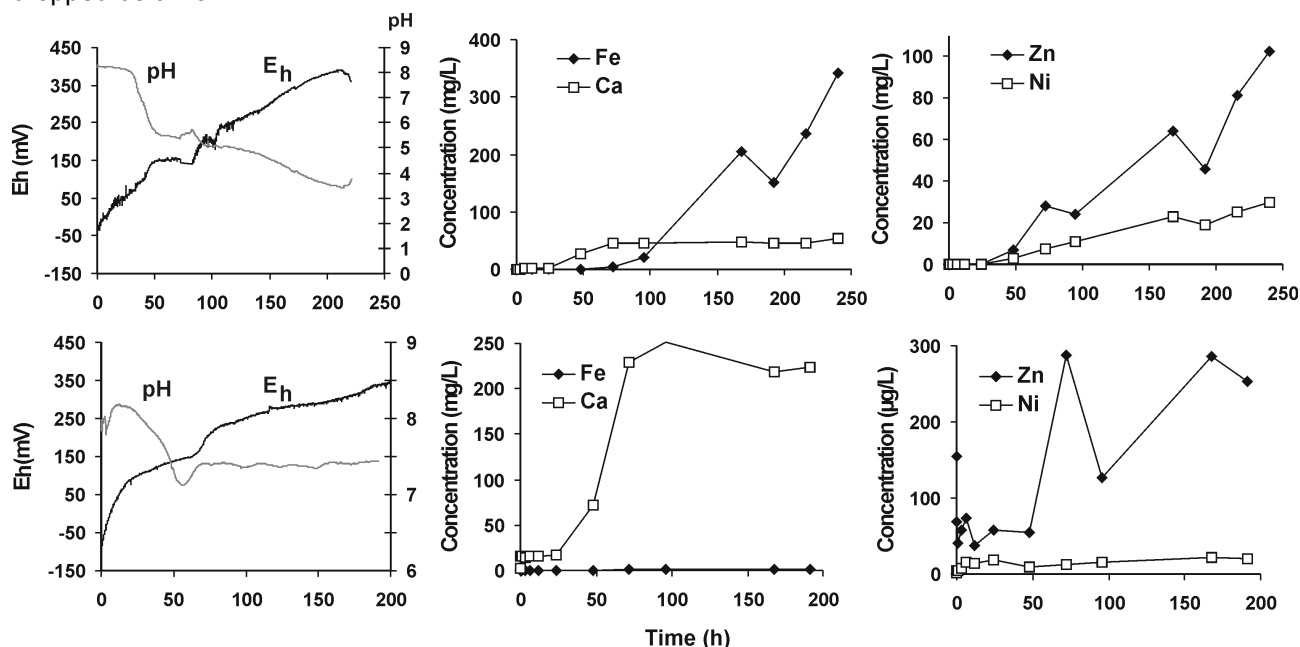


Figure 2 Evolution of pH and E_h , Ca-, Fe-, Zn- and Ni-concentrations during sediment resuspension (Liquid/Solid ratio = 10) of the Kogbeek (upper) and Upper Scheldt (lower).

3.1.1 Upper Scheldt

During resuspension, an increase in pH up to pH 8.2 was followed by a sharp pH-decrease between $t = 12$ h and $t = 48$ h to pH = 7.4 (Fig. 2). Redox potential was characterised by a gradual increase from -100 mV at $t = 0$ h to 340 mV at $t = 192$ h. At $t = 48$ h an increase in the amount of dissolved Ca, Fe and Zn was measured (Fig. 2). Other metals were only released in very low concentrations. From the amount of SO_4^{2-} released during resuspension (1959 mg/L) we can deduce that 6530 mg/kg S (as sulphide) was oxidised during resuspension. Compared to the evolution of porewater composition with time, the oxidation rate increased with a factor 10 during resuspension.

4 Discussion

4.1 Porewater composition

The composition of interstitial water is the most sensitive indicator of reactions that take place between pollutants, solid particles and the aqueous phase. For ecological considerations, the concentrations of metal species in the porewater are of primary importance because metal mobility and availability are related closely to the composition of the liquid phase (Brümmer, 1986). Although the Flemish legislation on soil remediation does not comprise Intervention Values for heavy metals in porewater, intervention values for heavy metals in groundwater (OVAM, 1995) can give an indication of the extent of the contamination. In sediment KB, Intervention values for Zn (500 µg/L) and Ni (40 µg/L) are exceeded from day 6, whereas Cd-, Cu-, Pb- and Cr-concentrations are above intervention values (5, 100, 20 and 50 µg/L respectively) after 15 days. In sediment US, it takes more than 20 days before Zn- and Ni-porewater concentrations exceed the intervention values.

Besides heavy metals, elevated concentrations of Ca, Al and Fe were measured in the porewater. Dissolution of CaCO₃ and Al- and Fe-(hydr)oxides are the most important buffer reactions in sediments (Calmano et al., 1993). During the oxidation of anoxic sediments, Fe also originates from the oxidation of Fe-sulphides. The strongest increase in SO₄²⁻ concentrations in sediment KB coincides with a sharp decrease in pH according to: HS⁻ + 4H₂O → SO₄²⁻ + 9H⁺ + 8e⁻. Calculations with MINTEQA2 (Allison *et al.*, 1991) indicate that the porewater is supersaturated with respect to CaSO₄·2H₂O (gypsum), suggesting that the precipitation of CaSO₄·2H₂O is responsible for the decrease in Ca-concentrations (Fig. 2) after ± 10 days.

4.2 Release rate of elements during oxidation

For most elements, concentrations in the porewater (Fig. 1) and in the suspension (Fig. 2) of sediment KB increased exponentially with time and a significant negative linear correlation was found between log(element concentration) and pH. Contrary to sediment US, which displays an elevated acid neutralizing capacity, the low pH that is reached after oxidation does not promote adsorption or coprecipitation of metals in sediments KB. The release of elements into the porewater of sediment KB as a function of time could be described with an exponential equation

$$C = a e^{kt} \quad (1)$$

where C (in mg/L, dimensionless in equation 1) is the concentration of element M in the porewater at time t (days) and a (dimensionless) and k (day⁻¹) are constants. The release rate, which is given by: dC/dt = ak e^{kt}, also increases exponentially with time. Although it is difficult to associate a physico-chemical model to this equation, the constant 'k' can be interpreted as a measure for the release rate.

Table 2 Release rate constant (k) of Zn, Ni, Cd, Co, Cu, Pb and Cr into the porewater and during resuspension of sediment KB. nf = no fit

	Zn	Ni	Cd	Co	Cu	Cr	Pb	Mn	Fe	Al
porewater										
k (day ⁻¹)	0.3	0.25	0.35	0.39	0.14	0.22	nf	0.18	0.26	0.28
r	0.98	0.93	0.95	0.96	0.87	0.87	nf	0.94	0.93	0.95
resuspension										
k (day ⁻¹)	1.01	0.74	0.74	0.98	0.33	0.42	0.53	0.77	1.02	0.63
r	0.95	0.9	0.96	0.92	0.84	0.96	0.97	0.92	0.97	0.91

4.3 Heavy metal migration into the underlying soil

In theory, the L/S ratios of a leaching test can be related to a time scale. This would require conversion of L/S to the amount of water (rainwater + floodwater) that penetrates into the soil underlying the dredged sediments disposed on land. The site specific solid tot liquid ratio (L/S_{site}) represents the cumulative solid tot liquid ratio that can be expected to contact the sediment layer over the estimated time period. According to Kosson et al. (1996), it can be estimated based on the infiltration rate, contact time, bulk density and height of the applied material.

$$LS_{\text{site}} = I \times t / (\rho \times h)$$

Where LS_{site} = the site-specific solid tot liquid ratio (L/kg)

I = infiltration rate (cm/year)

t = estimated time period (year)

ρ = material density (kg/cm^3)

h = material height (m)

Imagine that annually $500 \text{ L}/\text{m}^2$ penetrates into the soil. Sediment KB has an average bulk density $1,3 \text{ g}/\text{cm}^3$. When a sediment layer of 20 cm is considered, a L/S ratio of 10 is reached in 5.2 years. In a time span of 5.2 years, 146 mmol Zn and 10 mmol Ni will be released per kg of sediments (= amount of Zn and Ni released during resuspension of the oxidised sediment). Assuming that the underlying soil has a CEC of 150 mmol/kg and that the bulk density of the (ripened) dredged sediment and the underlying soil is identical, it is clear that the underlying soil will not be able to adsorb all the metals that are released from the sediment. The elevated amount of metals that are released from the dredged sediments will exceed the binding capacity of the soil, so that downward migration of heavy metals can be expected. Moreover, depth of the groundwater table is less than 5 m, so that there might be a risk for groundwater contamination.

4.4 Environmental risk and possible remediation

Oxidising conditions (by resuspension, dredging, overbank flooding) and the subsequent pH-decrease will cause a dramatic release of heavy metals from the sediment of the Kogbeek. Whereas heavy metals only appear in the porewater after 6 days, a considerable release of metals is already observed after 24 h of resuspension. Consequently, the resuspension experiment allows a faster evaluation of the potential impact of sediment oxidation on the environment.

Removal of the extremely polluted sediment is urgent since the sediment acts as a secondary source of pollution. However, in the case of urgent dredging operations, the temporary disposal of the sediment along the river is not recommended since extremely high metal concentrations will be released from the sediment. Considering the potential remediation of the sediment, bio-leaching could be a valuable option to remove Zn, Ni, Cd and Co. Two strategies can be applied for bio-leaching of metals from sediments. Intensive leaching is performed at low pH (<2.5), high concentrations of acids at short extraction times, while extensive leaching is performed at higher pH, low concentrations of acid and longer extraction times (> 80 hours) (Tichy et al., 1998).

Our experiments indicate that the 'natural' oxidation of the sediment in a confined disposal site will release an important amount of heavy metals, especially, Zn, Ni, Cd and Co. Therefore, aeration of the sediments

and washing with water can be considered as a first step in sediment remediation. The results of a simple water extraction (results not given) indicate that important amounts of Zn, Ni and Co can be released from the sediment by simply washing the ripened sediment with water. One overnight extraction with water (L/S = 20, 16 h) dissolves more than 70% of the total Zn-, Ni- and Cu-concentrations. Cu, Pb and Cr, however, are not significantly removed from the sediment by washing with water because these metals are more strongly bound to the sediment.

5 Conclusions and outlook

Heavy metal release from two contaminated sediments, which both belong to Class IV of the TRIADE classification (very bad global (physico-chemical, biological and ecotoxicological) sediment quality) was investigated.

Because of its important load of heavy metals, the considerable pH-decrease upon oxidation and its rather low capacity to bind heavy metals, the sediment from the Kogbeek is an obvious example of a chemical time bomb. During the first 6 days of simulated land-disposal, relatively low concentrations of Zn, Cd and Ni were released into the porewater. However, after 6 days exposure of the sediment to oxidising conditions, a sudden release of Zn, Cd, Ni, Cr, Pb and Cu was measured, together with a drastic pH-decrease from 8.0 to 3.5.

The sediment from the Upper Scheldt is characterised by a considerable acid neutralizing capacity and a lower production of H^+ during oxidation. pH remains around neutral after oxidation and this results in a much lower heavy metal mobility compared to the sediment of the Kogbeek.

Since dredged sediments can act as a chemical time bomb, the prediction of the fate of contaminants in dredged sediments is of primary importance. A faster oxidation of the sediment was obtained during the resuspension experiment. Monitoring the pH and the release of metals during sediment resuspension is an interesting tool for the evaluation of sediment quality upon dredging and oxidation. The amount of heavy metals released during resuspension can be used to predict the order of magnitude of heavy metal release into the porewater during simulated land-disposal.

The considerable amount of contaminated sediments that will be dredged in Europe in the coming years, asks for a tool to predict the evolution of sediment characteristics upon dredging. A rapid test, in which ripening and oxidation of river sediments are enhanced, can allow to assess the potential mobilisation of contaminants from dredged sediments. Future research will focus on the further development of such a test in order to establish a model for the quantification of metal release from dredged sediments.

6 References

- ALLISON JD, BROWN DS, NOVGRADAC KJ (1999) MINTEQA2/PRODEFA2, A chemical assessment model for environmental systems: version 4.0 user's manual. Environmental research laboratory office of research and development. US-EPA, Athens, 81 pp.
- BORMA LS, EHRLICH M, BARBOSA MC (2003) Acidification and release of heavy metals in dredged sediments. *Can Geotech J* 40: 1154-1163
- BROCKHOFF CA, CREED JT, MARTIN TD, MARTIN ER, LONG SE (1999) EPA Method 200.8, Revision 5.5: Determination of trace metals in waters and wastes by inductively coupled plasma-mass spectrometry, EPA-821R-99-017, October 1999, 61 pp.
- BRUMMER GW, GERTH J, HERMS U (1986) Heavy metal species, mobility and availability in soils. *Z. Pflanz Bodenk* 149: 382-398
- CALMANO W, HONG J, FÖRSTNER U (1993) Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Wat Sci Technol* 28(8-9): 223-235
- CAPPUYNS V, SWENNEN R, VERHULST J (2004a) Assessment of acid neutralizing capacity and potential mobilisation of trace metals from land-disposed dredged sediments. *Sci Total Environ* 333(1-3): 233-247

- CAPPUYNS V, SWENNEN R, DEVIVIER A (2004b) Influence of ripening on pH_{stat} leaching of heavy metals from dredged sediments. *J Environ Monit* 6(9): 774-781
- CHHABRA R, PLEYSIER J, CREMERS A (1975) The measurement of the cation exchange capacity and exchangeable cations in soils: a new method. In: *Proceedings of the International Clay Conference* (ed. SW Bailey), pp.439-449. Applied Publishing Ltd, Wilmette, IL.
- HEKSTRA GP (1995) Delayed effects of pollutants in soils and sediments: understanding and handling of chemical time bombs in Europe. *Ecoscript* 56. Amsterdam, Sticting Mondiaal Alternatief, 46 pp.
- JAPENGA J, SALOMONS W (1993) Dyke-protected floodplains: a possible chemical time bomb? *Land Degradation and Rehabilitation* 4: 373-380
- KOSSON DS, VAN DER SLOOT HA, EIGHMY TT (1996). An approach for estimation of contaminant release during utilization and disposal of municipal waste combustion residues *J Hazard Mat* 47(1-3): 43-75
- KUYPER R (1996) Ruimtelijke ordening en bodemverontreiniging in het landelijke gebied. *Chemische tijdbommen onder Nederland*. *Bodem* 2: 68-70
- LORS C, TIFFREAU C, LABOUDIGUE A (2004) Effects of bacterial activities on the release of heavy metals from contaminated dredged sediments. *Chemosphere* 56: 619-630
- NELSON DW, SOMMERS LE (1982) Total carbon, organic carbon and organic matter. In: AL Page, RH Miller, and DR Keeney (eds.), *Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties*. 2nd ed. American Society of Agronomy, Madison, pp. 516-593
- NEN 7349, 1995. Leaching characteristics of solid earthy and stony building and waste materials. Leaching tests. Determination of the leaching of inorganic components from granular materials with the cascade test. 1st edition, February 1995, Delft, 10pp.
- OVAM (1995) Vlaams reglement betreffende de bodemsanering - VLAREBO. Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest., Publicatienummer D/1995/5024/5, 63 pp.
- OVAM (2003) Ontwerp uitvoeringsplan Bagger- en Ruimingsspecie. Beleidsdocumenten afvalstoffen D/2003/5024/11, 2003, 206pp.
- PETERSEN W, WILLER E, WILLIAMOWSKI C (1997) Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. *Wat Air Soil Poll* 99: 515-522
- PROKOP Z, VANGEHELUWE ML, VAN SPRANG PA, JANSSEN CR, HOLOUBEK I (2003) Mobility and toxicity in sandy sediments deposited on land. *Ecotoxicology and Environmental safety* 34: 65-73.
- SEDNET (2003) The SedNet strategy paper. The opinion of SedNet on environmentally, socially and economically viable sediment management. TNO and Cranfield University (Eds.), 2003, 22 pp.
- SINGH SP, MA LQ, TACK FMG, VERLOO MG (2000) Trace metal leachability of land-disposed dredged sediments. *J Environ Qual* 29: 1124-1132
- STEPHENS SR, ALLOWAY BJ, CATER JE, PARKER A (2001) Towards the characterisation of heavy metals in dredged canal sediments and an appreciation of 'availability': two examples from the UK. *Env Poll* 113: 395-401
- STIGLIANI WM, DOELMAN P, SALOMONS W, SCHULIN R, SMIDT GRB, VAN DER ZEE SEATM (1991) Chemical time bombs. Predicting the unpredictable. *Environment* 33(4): 5-9, 26-30
- TICHY R, RULKENS WH, GROTENHUIS JTC, NYDLV, CUYPERS C, FAJTL J (1998) Bioleaching of metals from soils or sediments. *Wat Sci Technol* 37(8): 119-127
- VAN DER SLOOT H.A, RIETRA R, MULDER E (2002). Evaluatie van de gevolgen van de aanpassing van de pH van de uitloogvloei in de uitloognormen NEN 7343, 7345 en 7349. ECN-C-00-081, August 2000
- VAN HERREWEGHE S, SWENNEN R, CAPPUYNS V, VANDECASTEELE C (2002) Speciation of heavy metals and metalloids in soils: an integrated study near former ore treatment plants with emphasis on pH_{stat}-leaching. *J Geoch Expl* 76: 113-138
- VAN THUYNE G, BREINE J (2003) Visbestanden in enkele beken van het Maasbekken. Instituut voor Bosbouw and Wildbeheer. IBW.Wb.V.IR.2003.147, 12 pp.
- VLAAMSE MILIEUMAATSCHAPPIJ (2003). Waterbodemkwaliteit 2002, VMM, Aalst
- VOGEL AI (1961) Nephelometric determination of sulfate. In: Longman (ed.), *A Text-Book of Quantitative Inorganic Analysis*, 3rd edition, London, pp 850-851.